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(54) **Motor fuels of enhanced properties.**

(57) Environmentally-friendly fuels are provided comprising a gasoline fuel composition having a Reid vapor pressure (ASTM test method D-323) of 8.5 psi (58.6 kPa) or less, and preferably 8.0 psi (55.2 kPa) or less, containing up to 1/32 gram of manganese per gallon (0.008 g/liter) as at least one fuel-soluble cyclopentadienyl manganese tricarbonyl compound. Such motor fuels have improved octane quality as compared to the clear base fuel, and thus do not require the use of increased proportions of aromatics in the fuel. In addition, the motor fuels contribute to clean air by resulting in less evaporation into the atmosphere during such operations as storage and dispensing to vehicles and by resulting during engine operation in reduced emission of carbon monoxide (CO) and oxides of nitrogen ($NO_x$) while having little effect on the level of tailpipe hydrocarbon emissions. The fuels exhibit virtually no adverse effect upon exhaust gas catalysts of the type commonly used in present-day vehicles. Because the base fuels can contain reduced volumes of aromatics, the antiknock response of the fuels to the addition of the cyclopentadienyl manganese tricarbonyl compounds remains high.

EP 0 466 511 A1

This invention relates to gasoline fuel compositions having superior environmental and performance properties.

As is known, light ends of gasoline tend to evaporate into the atmosphere, especially during warm or hot weather; but removal of the light ends to reduce atmospheric pollution reduces the octane quality of the gasoline. Increased proportions of aromatic gasoline hydrocarbons of high octane quality, such as benzene, toluene, and xylene, can be used to compensate for this reduction in octane quality. However, since aromatics are not particularly desirable from the toxicological standpoint, it would be desirable to provide a way of reducing the front end volatility of gasoline without having to increase the aromatics content.

The gasoline fuel composition of this invention has a Reid vapor pressure (ASTM test method D-323) of 8.5 psi (58.6 kPa) or less, preferably 8.0 psi (55.2 kPa) or less, and contains up to 1/32 gram of manganese per gallon (0.008g/liter) as at least one fuel-soluble cyclopentadienyl manganese tricarbonyl compound. The use of cyclopentadienyl manganese tricarbonyls increases the octane quality of the low Reid vapor pressure gasoline without increasing its volatility and without requiring an increase in its aromatics content, and it has been found that these manganese compounds tend to exert a greater octane-improving effect in paraffinic and naphthenic hydrocarbons than they do in aromatic gasoline hydrocarbons. Moreover, the use of the fuels of the invention results in reduced emission of carbon dioxide and nitrogen oxides ($NO_x$) during engine operation while having little effect on the level of tailpipe hydrocarbon emissions; and they exhibit virtually no adverse effect upon exhaust gas catalysts and oxygen sensors of the type commonly used in present-day vehicles. Thus, the fuels of the invention are "environmentally friendly."

Other embodiments of the invention are improvements in (1) the normal process for preparing a gasoline by blending together appropriate proportions of suitable hydrocarbons of the gasoline boiling range [typically 70-440°F (21.1-226.7°C)] and/or (2) processes for distributing gasoline and/or dispensing it to motor vehicles.

In the improved preparation of the gasoline, the aforementioned cyclopentadienyl manganese tricarbonyl and low Reid vapor pressure fuel are blended in any suitable manner, e.g., by (a) blending the fuel-soluble additive into the gasoline during or after completion of the gasoline blending procedures or (b) mixing the additive with one or more streams of gasoline hydrocarbons or other blending components, such as oxygenated fuel blending components, before the streams are blended together. The octane-enriched gasoline thus obtained may then be stored in at least one storage tank in a tank farm, if desired, before being distributed for use in fueling motor vehicles; and it may then be dispensed to motor vehicles.

These improved processes lessen the amount of volatile hydrocarbons released into the atmosphere during storage and/or during fueling of a motor vehicle; and, in comparison with processes which utilize corresponding fuels containing no cyclopentadienyl manganese tricarbonyl, they reduce the amount of carbon monoxide and nitrogen oxides released into the atmosphere during operation of motor vehicles.

As noted above, the unleaded gasolines utilized in the practice of this invention must have a Reid vapor pressure of 8.5 psi (58.6 kPa) or below, and preferably 8.0 psi (55.2 kPa) or below. As is well known, Reid vapor pressures are determined at 100°F (37.8°C). Such gasolines are lead-free in the sense that no organolead antiknock agent is blended into the fuel, although they may contain trace amounts of lead contaminants. The hydrocarbonaceous gasoline base stocks that are used in forming the gasoline blends include straight run stocks, light naphtha fractions, cracked gasoline stocks obtained from thermal or catalytic cracking, hydrocracking, or similar methods, reformate obtained by catalytic reformation or like processes, polymer gasolines formed via polymerization of olefins, alkylates obtained by addition of olefins to isobutane or other hydrocarbons by alkylation processes, isomerates formed by isomerization of lower straight chain paraffins such as n-hexane, n-heptane, and the like, and other hydrocarbons of the gasoline boiling range formed by suitable refinery processing operations. Suitable amounts of appropriate hydrocarbons formed by other methods such as production from coal or shale can be included, if desired. For example reformates based on liquid fuels formed by the Fischer-Tropsch process can be included in the blends. In all cases, the resultant gasoline must satisfy the Reid vapor pressure requirements of this invention and additionally will possess the distillation characteristics typical of conventional regular, midgrade, premium, or super-premium unleaded gasolines. Thus the motor gasolines are generally within the parameters of ASTM D 4814 and typically have initial boiling points in the range of 70-115°F (21.1-46.1°C) and final boiling points in the range of 370-440°F (187.8-226.7°C) as measured by the standard ASTM distillation procedure (ASTM D 86). The hydrocarbon composition of gasolines according to volume percentages of saturates, olefins, and aromatics is typically determined by ASTM test procedure D 1319.

Generally, the base gasoline will be a blend of stocks obtained from several refinery processes. The final blend may also contain hydrocarbons made by other procedures such as alkylates made by the reaction of $C_4$ olefins and butanes using an acid catalyst such as sulfuric acid or hydrofluoric acid, and aromatics made from a reformer.

The saturated gasoline components comprise paraffins and naphthenates. These saturates are generally

obtained from: (1) virgin gasoline by distillation (straight run gasoline), (2) alkylation processes (alkylates), and (3) isomerization procedures (conversion of normal paraffins to branched chain paraffins of greater octane quality). Saturated gasoline components also occur in so-called natural gasolines. In addition to the foregoing, thermally cracked stocks, catalytically cracked stocks and catalytic reformates contain some quantities of saturated components.

Olefinic gasoline components are usually formed by use of such procedures as thermal cracking, and catalytic cracking. Dehydrogenation of paraffins to olefins can supplement the gaseous olefins occurring in the refinery to produce feed material for either polymerization or alkylation processes.

The gasoline gasoline base stock blends with which the cyclopentadienyl manganese tricarbonyl additive is blended pursuant to this invention will generally contain 40 to 80 volume % of saturates, 1 to 30 volume % olefins, and up to about 45 volume % aromatics. Preferred gasoline base stock blends for use in the practice of this invention are those containing no more than 40% by volume of aromatics, more preferably no more than 30% by volume of aromatics, still more preferably no more than 28% by volume of aromatics, and most preferably no more than 25% by volume of aromatics. Preferably, the overall fuel blend will contain no more than 1% by volume and most preferably no more than 0.8% by volume of benzene.

Particularly preferred unleaded gasolines produced and/or utilized in the practice of this invention not only meet the Reid vapor pressure criteria set forth hereinabove but in addition, are characterized by having (1) a maximum sulfur content of 300 ppm, (2) a maximum bromine number of 20, (3) a maximum aromatic content of 20% by volume, (4) a maximum content of benzene of 1% by volume, and (5) a minimum content of contained oxygen of 1% by weight in the form of at least one monoether or polyether, such gasoline having dissolved therein up to 1/32 gram of manganese per gallon (3.8 liters) as methylcyclopentadienyl manganese tricarbonyl. Gasolines of this type not containing the manganese additive are sometimes referred to as reformulated gasolines. See for example Oil & Gas Journal, April 9, 1990, pages 43-48.

From the standpoint of octane quality, the preferred gasoline base stock blends are those having an octane rating of (R + M)/2 ranging from 78-95.

Any of a variety of cyclopentadienyl manganese tricarbonyl compounds, e.g., those of U.S. Pat. No. 2,818,417, can be used in the practice of this invention. Illustrative examples of these manganese compounds include the cyclopentadienyl, methylcyclopentadienyl, dimethylcyclopentadienyl, trimethylcyclopentadienyl, tetramethylcyclopentadienyl, pentamethylcyclopentadienyl, ethylcyclopentadienyl, diethylcyclopentadienyl, propylcyclopentadienyl, isopropylcyclopentadienyl, tert-butylcyclopentadienyl, octylcyclopentadienyl, dodecylcyclopentadienyl, ethylmethylcyclopentadienyl, and indenyl manganese tricarbonyls, and mixtures of two or more such compounds. Generally speaking, the preferred compounds or mixtures of compounds are those which are in the liquid state of aggregation at ordinary ambient temperatures, such as methylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, liquid mixtures of cyclopentadienyl manganese tricarbonyl and methylcyclopentadienyl manganese tricarbonyl, and mixtures of methylcyclopenta dienyl manganese tricarbonyl and ethylcyclopentadienyl manganese tricarbonyl. The most preferred compound because of its commercial availability and its excellent combination of properties and effectiveness is methylcyclopentadienyl manganese tricarbonyl.

The practice of this invention and various embodiments thereof is illustrated by the following examples wherein the percentages of gasoline hydrocarbons are by volume. These examples are not intended to limit, and should not be construed as limiting, this invention.

## EXAMPLE 1

An unleaded motor gasoline blend is produced containing 58.9% saturated hydrocarbons, 17.5% olefinic hydrocarbons and 23.6% aromatic hydrocarbons, all of the gasoline boiling range. The Reid vapor pressure of the blend is 8.5 psi (58.6 kPa). With this base fuel are blended methylcyclopentadienyl manganese tricarbonyl to a concentration of 1/32 gram of manganese per gallon (0.008 g/liter) and 4-methyl-2,6-di-tert-butylphenol to a concentration of 7.5 pounds per thousand barrels (21.4 g/m$^3$). After storing the motor gasoline over water in a field storage tank on a tank farm, the product is transported by tank trucks to gasoline filling stations where it is dispensed on demand to motor vehicles. The vehicles consume the same during their operation.

## EXAMPLE 2

An unleaded motor gasoline of this invention is produced to contain 56.9 saturates, 20.0% olefins and 23.1% aromatics, all of the gasoline boiling range. The components are selected such that the Reid vapor pressure of the blend is 8.4 psi (57.9 kPa). A mixture of tertiary butylated phenolic antioxidants containing 85% by weight of 2,6-di-tert-butylphenol is blended into the fuel to a concentration of 6.5 pounds per thousand barrels

( 18.5 g/m$^3$). Methylcyclopentadienyl manganese tricarbonyl is blended into the resultant blend to a concentration of 1/32 gram of manganese per gallon (0.008 g/liter). This fuel is stored, transported, and dispensed to and utilized in the operation of motor vehicles, the majority of which contain catalytic converters.

EXAMPLE 3

Into an unleaded motor gasoline (67.7% saturates, 7.5% olefins, 24.8% aromatics) having a Reid vapor pressure of 8.0 are blended methylcyclopentadienyl manganese tricarbonyl and methyl tert-butyl ether in amounts such that the resultant fuel contains 1/32 gram of manganese per gallon (0.008 g/liter) and 2.7% by weight of oxygen as methyl tert-butyl ether. The finished fuel, which can contain, and preferably does contain, conventional amounts of antioxidant, metal deactivator, and carburetor detergent, is dispensed to and utilized in the operation of motor vehicles including passenger cars, buses, trucks, vans, and motorcycles.

EXAMPLE 4

Examples 1-3 are repeated except that in one case the respective motor fuels contain 1/40 gram of manganese per gallon (0.007 g/liter), in another the respective motor fuels contain 1/50 gram of manganese per gallon (0.005 g/liter), in a third case, 1/64 gram of manganese per gallon (0.004 g/liter) and in still another case, 1/100 gram of manganese per gallon (0.003 g/liter).

EXAMPLE 5

Examples 1-4 are repeated except that in each case the methylcyclopentadienyl manganese tricarbonyl is replaced by an equal concentration of manganese as cyclopentadienyl manganese tricarbonyl.

EXAMPLE 6

Examples 1-4 are repeated except that in one series of cases the respective fuels contain instead of methylcyclopentadienyl manganese tricarbonyl, a mixture of 90% by weight of methylcyclopentadienyl manganese tricarbonyl and 10% by weight of cyclopentadienyl manganese tricarbonyl in amounts such that the respective fuels contain the same respective concentrations of manganese as the fuels of Examples 1-4. In another series of cases, the respective fuels of Examples 1-4 contain the same respective concentrations of manganese in the form of dimethylcyclopentadienyl manganese tricarbonyl in lieu of the methylcyclopentadienyl manganese tricarbonyl. And in still another series of cases the specified concentrations of manganese in the fuels of Examples 1-4 are supplied by tert-butylcyclopentadienyl manganese tricarbonyl. In yet another series of cases the manganese additive used in forming the motor fuel compositions is indenylmanganese tricarbonyl instead of methylcyclopentadienyl manganese tricarbonyl.

EXAMPLE 7

With an unleaded gasoline formulated to contain 40.1% saturates, 15.3% olefins, and 44.6% aromatics and having a Reid vapor pressure of 8.3 psi (57.2 kPa) are blended the following components:

5 pounds per thousand barrels (14.3 g/m$^3$) of a phenolic mixture composed of 75 % 2,6-di-tert-butylphenol, 10-15 % 2-tert-butylphenol and 10-15 % of 2,4,6-tri-tert-butylphenol; and

1 pound per thousand barrels (2.9 g/m$^3$) of N,N'-disalicylidene-1,2-propanediamine.

Thereafter, methylcyclopentadienyl manganese tricarbonyl is blended into the gasoline to a concentration equivalent to 1/32 gram of manganese per gallon (0.008 g/liter).

EXAMPLE 8

An unleaded motor gasoline blend having a Reid vapor pressure of 7.8 psi (53.8 kPa) is formulated from 72.5% saturates, 4.0% olefins, and 23.5% aromatics (of which less than 3% by volume is benzene so that the fuel contains less than 1% by volume of benzene). Methyl tert-butyl ether is blended into the base gasoline in amount sufficient to provide an oxygen content of 2.0% by weight in the fuel. Thereafter methylcyclopentadienyl manganese tricarbonyl is blended into the resultant motor fuel in an amount equivalent to 1/35 gram of manganese per gallon (0.008 g/liter).

EXAMPLE 9

Example 8 is repeated with the exceptions that (a) the initial gasoline blend has a Reid vapor pressure of 7.9 psi (54.5 kPa) and is composed of 75.7% saturates, 4.8% olefins, and 19.5% aromatics (of which aromatics, less than 3.5% by volume is benzene), and (b) a mixture of methyl tert-butyl ether and ethyl tert-butyl ether is blended into the fuel in an amount such that the content of the oxygenated fuel blend is equivalent to 2.5% by weight of oxygen.

EXAMPLE 10

Example 8 is again repeated except that (a) the initial gasoline blend has a Reid vapor pressure of 7.7 psi (53.1 kPa) and is composed of 78.6% saturates, 4.4% olefins and 17.0% aromatics (the entire fuel blend again containing less than 1% by volume of benzene); and (b) in lieu of methyl tert-butyl ether, tert-amyl methyl ether is blended into the gasoline in an amount equivalent to an oxygen content in the fuel of 2.7% by weight.

EXAMPLE 11

Blended with the respective fuels of Examples 7-10 at a concentration level of 100 pounds per thousand barrels, (285.3 g/m$^3$) is a polyether amine deposit control additive available commercially from Oronite Chemical Co. as OGA-480.

EXAMPLE 12

Blended with the respective fuels of Examples 7-10 at a concentration of 100 pounds per thousand barrels (285.3 g/m$^3$) is a polyalkenyl succinimide deposit control additive available commercially from Ethyl Petroleum Additives, Ltd. as HITEC 4450 additive.

EXAMPLE 13

Blended with the respective fuels of Example 7-10 at a concentration level of 100 pounds per thousand barrels (285.3 g/m$^3$) is a polyisobutenyl amine deposit control additive available commercially from Oronite Chemical Co. as OGA-472.

As can be appreciated from the above examples, the fuels of this invention can, and preferably do, contain additives in addition to the cyclopentadienyl manganese tricarbonyl compound or compounds. Such other additives include antioxidants, deposit-control additives (also known as induction system cleanliness additives or fuel detergents), and oxygenated materials such as dialkyl ethers, all with the proviso that the volatility of such materials does not cause the fuel to exceed the Reid vapor pressure limitations required pursuant to this invention. Other additives that may be employed include supplemental antiknock additives such as aromatic amine antiknocks such as N-methyl aniline; iron antiknock compounds such as ferrocene, methylferrocene, and butadiene iron tricarbonyl; and nickel antiknock compounds such as cyclopentadienyl nickel nitrosyl. Corrosion inhibitors, metal deactivators, demulsifiers, and dyes comprise other types of additives that can be employed.

Preferred oxygenated materials that can be, and preferably are, blended into the fuels of this invention are ethers of suitable low volatility such as methyl tert-butyl ether, ethyl tert-butyl ether, tert-amyl methyl ether, and 2,2-diethyl- 1,3-propanediol. Also useful are fuel-soluble esters and alcohols of suitably low volatility such as tert-butyl acetate, 1-hexanol, 2-hexanol, 3-hexanol, and polyethoxyethanols. Usually such oxygenated compounds are employed in amounts sufficient to provide up to 3 to 4 weight % oxygen in the fuel, provided such usage is consistent with existing or proposed legislation. Other suitable oxygen-containing blending agents include p-cresol, 2,4-xylene, 3-methoxyphenol, 2-methylfuran, cyclopentanone, isovaleraldehyde, 2,4-pentanedione and similar oxygen-containing substances.

Preferred antioxidants for the fuels of this invention are hindered phenolic antioxidants, such as 2,6-di-tert-butyl-phenol, 2,4-dimethyl-6-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-butyl-2,6-di-tert-butylphenol, and mixtures of tertiary butylated phenols predominating in 2,6-di-tert-butylphenol. In some cases aromatic amine antioxidants can prove useful either alone or in combination with a phenolic antioxidant. Antioxidants are usually employed in amounts of up to 25 pounds per thousand barrels (71.3 g/m$^3$), the amount used in any given case being dependent upon the stability (e.g., olefin content) of the gasoline

Another type of additives preferably utilized in the fuels of this invention are ashless detergents such as polyether amines, polyalkenyl amines, alkenyl succinimides, polyether amide amines, and the like. Such mate-

rials can be used at treat levels of 50 to 500 pounds per thousand barrels (142.6-1426.4 g/m$^3$), and more usually in the range of 100 to 200 pounds per thousand barrels (285.3-570.6 g/m$^3$).

The cyclopentadienyl manganese tricarbonyl compounds as well as the other supplemental additives or blending agents can be blended with the base fuels according to well known procedures utilizing conventional mixing equipment. This invention is directed to all such fuel compositions meeting the primary requisites of this invention.

Driving tests were conducted on a 48-car fleet for a total of more than three million test miles (4.8 x $10^6$ km). Half of the cars of each model group were run on "clear" (i.e., manganese additive-free) test fuel. The other half were run on the same fuel containing 1/32 of a gram of manganese per gallon (0.008 g/liter) as methylcyclopentadienyl manganese tricarbonyl. The inspection data on the base fuel are set forth in the following table.

HOWELL EEE TEST FUEL

| | ASTM Method | Certification Fuel Specifications Min. | Certification Fuel Specifications Max. | Typical Properties |
|---|---|---|---|---|
| Gravity, API | D 1298 | | | 59.2 |
| Reid Vapor Pressure, psi | D 323 | 8.7 | 9.2 | 9.2 |
| Sulfur, wt. % | D 3120 | | 0.20 | 0.001 |
| Lead, g/gal. | D 3237 | 0.0 | 0.05 | 0.001 |
| Phosphorus, g/gal. | D 3120 | | 0.20 | Nil |
| Distillation, °F | D 86 | | | |
| IBP | | 75 | 95 | 92 |
| 10% | | 120 | 135 | 128 |
| 50% | | 200 | 230 | 218 |
| 95% | | 300 | 325 | 313 |
| End Point | | | 415 | 373 |
| Hydrocarbon Composition | D 1319 | | | |
| Saturates, Vol. % | | | | 66.5 |
| Olefins, Vol. % | | | 10 | 1.8 |
| Aromatics, Vol. % | | | 35 | 31.7 |
| Existent Gum, mg/100 ml | D 381 | | | 0.8 |
| Copper Strip Corrosion | D 130 | | | 1 |
| Research Octane Number | D 2699 | 93.0 | | 96.8 |
| Motor Octane Number | D 2700 | | | 88.5 |

After fleet cars had accumulated 75,000 miles (120,701 km), they were analyzed for catalyst conversion efficiency -- i.e., the ability of automobile catalysts to convert the regulated emissions of hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxide ($NO_x$) to non-regulated materials. When compared with conversion efficiencies of catalysts run on clear test fuel, those run with the manganese-containing fuel were found to be essentially the same for HC, approximately 1.1 percentage points better for CO, and 3.3 percentage points better for $NO_x$.

Fleet cars were checked after 50,000 miles (80,467 km) for performance of oxygen sensors. For each model, the oxygen sensors were removed from each automobile and individually tested. No significant difference occurred in performance of the oxygen sensors from cars run on the clear fuel versus cars run on the same fuel containing the manganese additive.

Fleet cars were also tested at the end of 75,000 miles (120,701 km) to determine if catalyst plugging occurred. This was done by measuring the pressure level of the exhaust before it enters the catalyst. There was no evidence of catalyst plugging on any of the vehicles.

While the base fuel used in the above tests did not comply with the Reid vapor pressure requirements pursuant to this invention, the above tests indicate that cyclopentadienyl manganese tricarbonyl compounds when used in the concentrations herein specified, do not cause catalyst plugging nor degrade the performance of the automobile emission systems. Thus by reducing the Reid vapor pressure of the fuel to the levels specified herein, all of the foregoing benefits can be achieved while at the same time reducing the extent to which light ends of the gasoline are vaporized into the atmosphere during storage, transportation, and fuel dispensing operations.

## Claims

1. An unleaded gasoline fuel composition having a Reid vapor pressure (ASTM test method D-323) of 8.5 psi (58.6 kPa) or less containing up to 1/32 gram of manganese per gallon (0.008 g/liter) as at least one fuel-soluble cyclopentadienyl manganese tricarbonyl compound.

2. A composition as claimed in Claim 1 wherein the Reid vapor pressure of the gasoline is 8.0 psi (55.2 kPa) or less.

3. A composition as claimed in Claim 1 or Claim 2 wherein said at least one fuel-soluble cyclopentadienyl manganese tricarbonyl compound consists essentially of methylcyclopentadienyl manganese tricarbonyl.

4. A composition as claimed in Claim 1, 2, or 3 wherein the base gasoline contains no more than 25% by volume of aromatic hydrocarbon components and less than 1% by volume of benzene.

5. A composition as claimed in any of the preceding claims wherein the base gasoline contains at least 50% by volume of saturated hydrocarbon components.

6. A composition as claimed in any of the preceding claims wherein the fuel composition additionally contains up to about 4% by weight of oxygen as at least one oxygenated fuel blending component.

7. An unleaded gasoline fuel composition which comprises a gasoline fuel having (1) a Reid vapor pressure (ASTM test method D-323) of 8.5 psi (58.6 kPa) or less, (2) a maximum sulfur content of 300 ppm, (3) a maximum bromine number of 20, (4) a maximum aromatic content of 20% by volume, (5) a maximum content of benzene of 1% by volume, and (6) a minimum content of contained oxygen in the form of at least one monoether or polyether of 1% by weight, said gasoline having dissolved therein up to 1/32 gram of manganese per gallon (0.008 g/liter) as methylcyclopentadienyl manganese tricarbonyl.

8. In a process for the production of gasoline, the improvement which comprises forming a base unleaded gasoline having a Reid vapor pressure (ASTM test method D-323) of 8.5 psi (58.6 kPa) or less and providing therein up to 1/32 gram of manganese per gallon (0.008 g/liter) as at least one fuel-soluble cyclopentadienyl manganese tricarbonyl compound.

9. In a process for the production and distribution of gasoline, the improvement which comprises forming unleaded gasoline having a Reid vapor pressure (ASTM test method D-323) of 8.5 psi (58.6 kPa) or less, providing therein up to 1/32 gram of manganese per gallon (0.008g/liter) as at least one fuel-soluble cyclopentadienyl manganese tricarbonyl compound to form an octane enhanced gasoline, and storing said octane-enhanced gasoline in at least one storage tank in a tank farm prior to distributing the octane-enhanced gasoline for use in fueling motor vehicles.

10. In a process for dispensing gasoline to motor vehicles, the improvement which comprises dispensing to motor vehicles unleaded gasoline having a Reid vapor pressure (ASTM test method D-323) of 8.5 psi (58.6 kPa) or less and containing up to 1/32 gram of manganese per gallon (0.008 g/liter) as at least one fuel-soluble cyclopentadienyl manganese tricarbonyl compound.

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number

EP 91 30 6359

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.5 ) |
|---|---|---|---|
| X<br>Y | WO-A-8 701 384 (ORR)<br>* the whole document * | 1-6,8-10<br>7 | C10L1/30<br>C10L1/14<br>C10L1/02 |
| Y | FR-A-1 140 411 (GULF RESEARCH & DEVEL.)<br>* page 6, column 1 * | 7 | |
| X | US-A-4 139 349 (PAYNE)<br>* the whole document * | 1-3,5,<br>8-10 | |
| A | US-A-4 005 993 (NIEBYLSKI ET AL.)<br>* the whole document * | 1-10 | |
| D,A | US-A-2 818 417 (BROWN ET AL.)<br>* the whole document * | 1-10 | |
| D,A | OIL AND GAS JOURNAL.<br>April 9, 1990, TULSA US<br>pages 43 - 48;<br>UNZELMAN: 'REFORMULATED GASOLINES WILL CHALLENGE PRODUCT-QUALITY MAINTENANCE '<br>* the whole document * | 1-10 | TECHNICAL FIELDS SEARCHED (Int. Cl.5 )<br>C10L |
| A | GB-A-1 145 930 (ESSO)<br>* page 4; table 2 * | 4,7 | |
| A | US-A-2 609 279 (MORRIS ET AL.)<br>* the whole document * | 7 | |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 26 SEPTEMBER 1991 | DE LA MORINERIE |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
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EPO FORM 1503 03.82 (P0401)